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RESEARCH RELATED TO MEASUREMENTS OF ATOMIC SPECIES IN THE EARTH'S UPPER ATMOSPHERE

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Introduction

Precise analysis by rocket- and satellite-borne mass spectrometers of the concentration of atomic oxygen in the earth's upper atmosphere is seriously impeded by the reactive character of the oxygen itself. Gaseous atomic oxygen is a highly reactive species that is known to interact with solid surfaces by adsorption, by chemical reaction forming a stable solid oxide phase, and by recombining with sorbed oxygen atoms to produce gaseous molecular oxygen. Hence, the oxygen atom concentration as seen by a mass spectrometer may be substantially different from that of the environment due to atom removal on the surfaces of the instrument. The objective of this project is to elucidate the kinetics and mechanism that are associated with the interaction of oxygen atoms with various solid surfaces under conditions similar to those encountered in the upper atmosphere.

The same difficulties encountered in the determination of O/O_2 ratios in the upper atmosphere also interfere with analyzing these entities in a laboratory experiment. To minimize such perturbations, the approach used in this study is to measure changes in oxygen atom concentration resulting from surface reaction and recombination in an environment where changes in both the oxygen pressure and the rate of production of oxygen atoms are negligible.

Theoretical Basis of the Study

A basic requirement of this study is that the pressure environment of the surfaces of interest be comparable to that of the atmosphere in the region 200 miles above the earth. This condition demands that the experiments be carried out in an ultrahigh vacuum system that is capable of attaining base pressures of 10^{-9} torr or lower. At such pressures, adsorption and desorption of gaseous species from every surface within the vacuum system are likely to contribute formidably to the composition of the gas phase. This is particularly true of the gaseous components that are of primary interest, viz., atomic and molecular oxygen. Hence, the experimental apparatus has been designed so that measurements can be made when all surfaces are in a steady state condition with respect to adsorption and desorption.

The fundamental parameter to be measured in this study is the rate of interaction of oxygen atoms with a specimen of the material of interest as a function of the gas-phase density of atomic and molecular oxygen. The basic analytical tool to be employed is a quadrupole residual gas analyzer. However, interpreting gas-phase compositions reported by this device depends on a clear understanding and control of the dynamic steady state with respect to gas-surface interaction within the entire vacuum system.

Such conditions will be provided by the experimental apparatus being assembled, which is depicted schematically in Fig. 1. This equipment is essentially a three-chambered vessel. Chambers A and B and B and the pump, D, are joined by conductances F and f, respectively. Molecular oxygen is supplied to chamber A through a servo-controlled valve at a sufficient rate to maintain a constant pressure in chamber B. Oxygen atoms are generated on a heated platinum filament in chamber B at the rate R_0. The rate of removal of species by sorption on the walls and other surfaces within the apparatus is designated R_w. The specimen is situated in chamber C, which communicates with chamber B through a large conductance when glass shutter No. 1 is open. Chamber C may be separately evacuated by opening shutter No. 2. Oxygen atom recombination on the specimen in effect makes this surface a source of molecular oxygen; here the rate of formation of O_2 is termed R_{O_2}.

Based on a steady-state balance between the influx and efflux of molecular oxygen in chamber B, the following flow equations may be written. P represents the pressure of O_2 in the chamber identified by the subscript.

	Flow Rate of O_2 into System				Flow Rate of O_2 out of System					
	Inlet Conductance F	+	Atom Recombination on Specimen	=	Pump Conductance f	+	Surface Pumping	+	Atom Generation on Filament	
Initial conditions (shutter No. 1 closed)	$F(P_A - P_B)$			=	$f(P_B - P_D)$	+	R_{WB}	+	$\frac{1}{2}R_O$	(1)
Final conditions (shutter No. 1 open)	$F(P'_A - P_{BC})$	+	R_{O_2}	=	$f(P_{BC} - P_D)$	+	R_{WBC}	+	$\frac{1}{2}R_O$	(2)

By employing a pump of high speed that is throttled by conductance f, $P_B \gg P_D$ and the latter term may be neglected. Analysis of the system is further simplified by operating in the constant pressure mode so that $P_B = P_{BC}$, and R_O is constant. Combining Equations (1) and (2) gives

$$R_{WB} - R_{WBC} - F(P_A - P'_A) = -R_{O_2} \tag{3}$$

The effect of the wall in chamber C on atom removal can be evaluated in a blank experiment in which there is no specimen in chamber C. Under such conditions

$$R_{WB} - R_{WBC} = F(P_A - P'_A)$$

Since F, P_A, and P'_A are measurable parameters, R_{O_2} may be evaluated for any catalytic specimen placed in chamber C by means of Eq. (3). Evaluating R_{O_2} as a function of the partial pressures of atomic and molecular oxygen will reveal the kinetics of the steady-state recombination process and will provide insight into the mechanism. A similar analysis, of course, may be derived in terms of atomic oxygen instead of molecular oxygen.

Observing the rate of interaction of atomic oxygen during the first moment of exposure of a clean metallic surface is also of interest. Measurements of the transient variation in O/O_2 ratios between initial and final steady states when shutter No. 1 is opened will indicate such interaction kinetics, unless resolution of the processes is obscured by pressure pulses associated with operation of the mechanical components of the system.

Experimental Considerations

The relative magnitudes of the various atom generation and removal terms cannot be accurately predicted in advance of an experimental measurement. The catalytic characteristics of many materials for oxygen atom recombination at higher pressures have been studied and were employed as a basis for designing the present experimental apparatus. In general, metals exhibit an order of magnitude higher level of catalytic activity than glass. Hence, chamber C (Fig. 1), containing the catalytic specimen, is constructed entirely of glass, including the shutters. The initially investigated specimens will be silver, gold, and platinum wires, which, based on existing knowledge, represent a spectrum of recombination and reactivity characteristics. The wire will be mounted on glass-shielded electrical leads so that, before exposure to oxygen atoms, the surface can be cleaned by passing an electric current through it. The initial encounter of oxygen atoms, therefore, will be with a clean metallic surface. The nature of this interaction may well involve chemical reaction between the gaseous oxygen atoms and lattice atoms of the metal. Measurements of the kinetics of atom removal as a function of coverage will contribute to an understanding of this process.

The apparatus is currently in the final stages of assembly. A photograph of the vacuum system is shown in Fig. 2. Testing and initial measurements are expected to commence within the month.

Personnel

Staff members who have participated in this program during the past quarter include: Bjorn W. Bergsnov-Hansen, Noboru Endow, Leon E. Hiam, Jan W. Van Gastel, Henry Wise, and Bernard J. Wood.

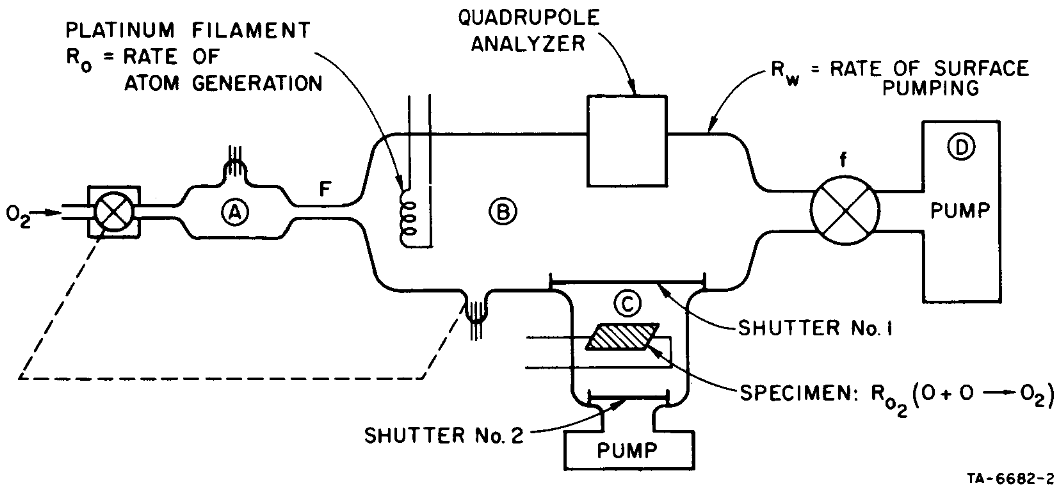

FIG. 1 SCHEMATIC DIAGRAM OF EXPERIMENTAL APPARATUS

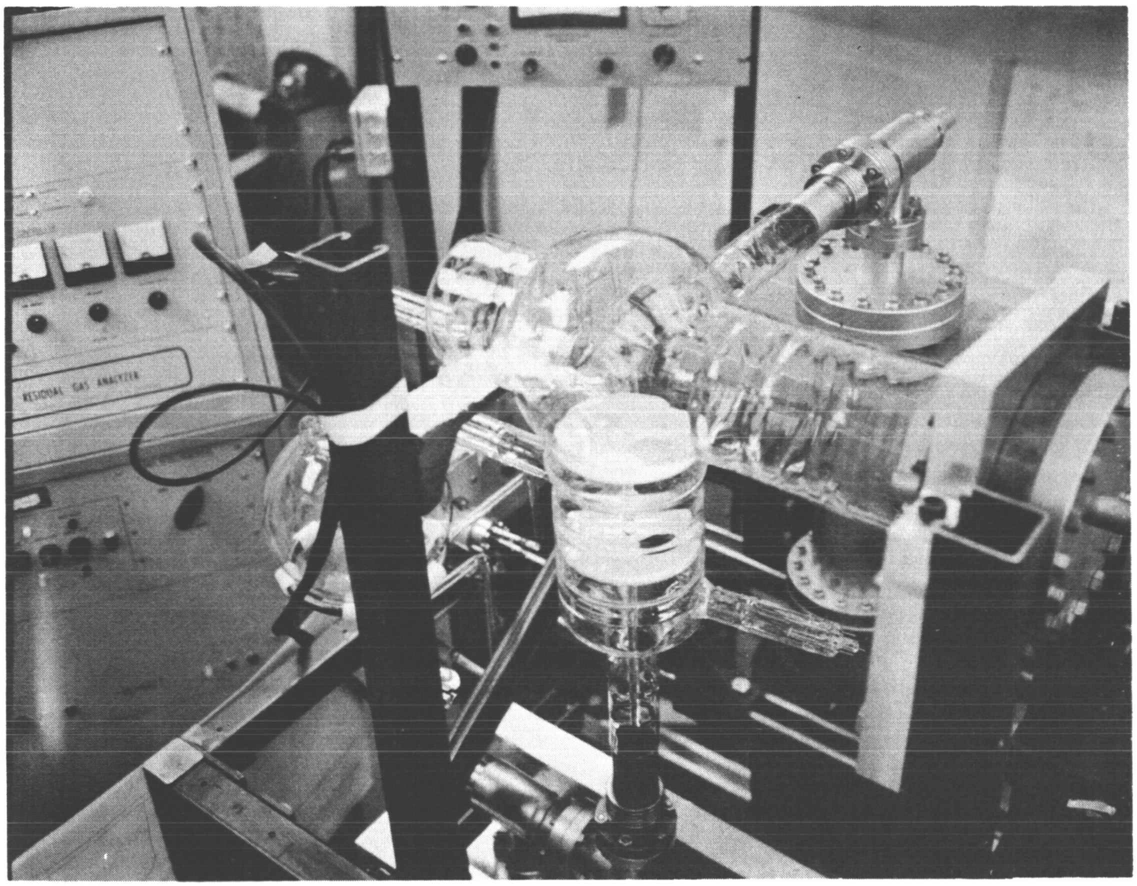

FIG. 2 PHOTOGRAPH OF APPARATUS. Specimen chamber C located between circular glass plate shutters